# *Ab Initio* to activity: Machine learning assisted optimization of high-entropy alloy catalytic activity.

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## Abstract

High-entropy alloys are slowly making their debut as a platform for catalyst discovery, but conventional methods, theoretical as well as experimental, may fall short of screening the vast composition space inhabited by this class of materials. New theoretical approaches are needed to gauge the catalytic activity of high-entropy alloys and optimize the alloy composition within a feasible time frame as a prerequisite for further experimental studies.

Herein, we establish a workflow for simulations of catalysis on high-entropy alloy surfaces. For each step of the modeling we present our choice of method, however, we also acknowledge that alternative options are available.

We apply the developed methodology to predict the net catalytic activity of any alloy composition, within the composition space spanned by Ag-Ir-Pd-Pt-Ru, for the oxygen reduction reaction. Based on first-principle calculations, a graph convolution neural network is used to predict adsorption energies of \*OH and \*O. Subsequently, taking competitive co-adsorption of reaction intermediates into account, we couple the net adsorption energy distribution of a high-entropy alloy surface to the expected current density. Lastly, this procedure is used in conjunction with a Bayesian optimization scheme to search for optimal alloy compositions, which yields several promising compositions.

This result shows that an unbiased *in silico* pre-screening and discovery of catalyst candidates is viable and will help scale the otherwise insurmountable challenge of searching for high-entropy alloy catalysts. It is our hope that our computational framework, which is freely available on GitHub, will aid other research groups to efficiently identify promising high-entropy alloy catalysts.

<u>Keywords:</u> high-entropy alloy electrocatalysis, oxygen reduction reaction, density functional theory, graph convolutional neural network, adsorbate coverage, bayesian optimization.

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<u>Data availability</u>: A working example of all steps used in this work is freely available at our repository in Github along with guidance for use in other projects: <u>https://github.com/jkpedersen/heacs</u>

## Introduction

High-entropy alloys (HEAs) and complex solid solutions hold great potential for catalyst discovery [1-7] because the metal surfaces can be tuned to maximize the likelihood of ideal binding sites for specific reactions in accordance with the Sabatier principle [8]. However, the huge composition space available to these materials presents a challenge to any rational discovery procedure, as the selection of constituent elements and ratios makes experimental screening virtually impossible. Some experimental high-throughput methods can screen many hundred compositions at once, but these points in the high dimensional composition space are typically positioned on relatively small, bounded hyperplanes [9-11].

Therefore, simulation-guided screenings are evidently needed, but the stochastic nature of the atomic surface environments demands a new approach to theoretical modeling. The canonical process of catalytic theory has been to utilize quantum-mechanical calculations to model the relative energies of specific surface structures and adsorption sites. These structures have been selected because of the vital role they are thought to have in certain reactions e.g. undercoordinated Cu-sites for the  $CO_2$  reduction reaction [12-15]. The energies have been used to establish theoretical frameworks to guide our understanding of catalytic activity and surface-adsorbate interaction e.g. the Brønsted–Evans–Polanyi principle [16-18] or scaling relations [19,20].

In the regime of HEAs we cannot solely consider specific structures or sites as the surface will have a diverse selection of available sites [12,21-23]. An illustration of this point is the threefold-coordination of an oxygen atom to a face-centered cubic (fcc) (111) surface, of which a quinary solid-solution alloy would result in 35 different possible adsorption sites before even accounting for the influence of neighboring atoms. Therefore, we instead consider the probability distribution of possible sites and their differing surface properties, such as the adsorption energy of reaction intermediates, which can then be coupled to an expected catalytic activity via established theory [24].

However, due to the vast number of unique binding sites, even on simple alloys, quantum-mechanical calculations of energies are not feasible and we must turn to regression of adsorption energies. We propose that a precise adsorption energy regression algorithm, together with effects of co-adsorption of multiple species, will make it possible to rapidly gauge the catalytic activity of an HEA surface given a specific composition.

In this paper, we describe our computational framework for HEA catalyst discovery as illustrated in figure 1. From sampling the composition space with density functional theory (DFT) calculations to a predictive measure of the net catalytic activity and lastly optimization of the alloy composition. We discuss some of the necessary modeling choices involved in the process and some alternative options for selected modeling steps.

As a relevant system we target the composition space spanned by the HEA Ag-Ir-Pd-Pt-Ru, which has previously been successfully synthesized [25,26], and seek an optimum catalyst for the oxygen reduction reaction (ORR). However, this choice is exemplificatory and any descriptor-based reaction could be modeled. We demonstrate our sampling strategy and employ a neural network to predict the adsorption energy distributions of ontop and fcc

hollow bound \*OH and \*O (asterisk indicating coordination to the metal surface) on the fcc(111) facet. These specific adsorbate/site combinations have been widely used as descriptors for the observed catalytic activity of ORR [21,22,25,27]. Subsequently, we adjust these energy distributions due to co-adsorption and couple these to a catalytic activity estimate. A Bayesian optimization routine is finally employed to find alloy compositions with high estimated catalytic performances.



**Fig. 1** Overview illustrations of the workflow towards alloy optimization from left to right. **a**) Choice of HEA constituent elements. **b**) Sample binding sites with DFT methods. **c**) Train regression algorithm for adsorption energy prediction. **d**) Predict the net adsorbate coverage and distributions of adsorption energies. **e**) Estimation of catalytic activity based on the net adsorption energy distributions. **f**) Searching the composition space for optima calling steps **d** and **e** for each composition screened.

# Sampling the HEA surface

To characterize the adsorption energy distributions of the myriads of different adsorption sites on the HEA surface, we need to establish an initial screening to base our analysis on. We have chosen to apply standard GGA-DFT methods to calculate the energies as these have proven to be the best compromise between accuracy and computational cost and have widely been the basis of theoretical catalyst discovery for decades [28].

To capture the local electronic environment that determines the adsorption energy, the unit cell must be of sufficient size. 3x3 atom-sized surfaces have adequate lateral dimensions to incorporate the immediate neighboring atoms coordinated to the binding site of monodentate adsorbates. These atomic positions have the highest contribution to the electronic effect perturbing the adsorption energy [29], and by using 3x3 atom-sized surfaces we also sample asymmetric binding motifs which would otherwise be excluded by using a 2x2 atom-sized surface. Additionally, we have earlier observed the electronic effect of atomic positions in the third layer to propagate in a long-ranged and direction-dependent manner and for this effect to adequately converge we use slabs with 5 atomic layers [29].

Another well known feature that affects adsorption energy is surface strain [30-33]. In simulated HEA surfaces, this could be problematic as the simulated slab with periodic boundary conditions is part of a thought up extended surface with a crystal lattice corresponding to the weighted mean of element fractions not yet determined [34]. However, the inherent lattice distortion of HEAs, which we have observed to be a countermeasure to the surface strain [30], presents a solution: Since the simulated slab is nested in a surface that can accommodate lattice distortion, the adsorption energy is most accurately reproduced when the unit cell's lateral dimensions are scaled to the weighted average lattice constant of the elements constituting the slab surface. This emulates the lattice distortion of the local atomic environment. By geometry optimizing each slab this way, any strain

correction of energies is avoided when regressing the adsorption energies of sites on surfaces with other elemental compositions than what each slab was sampled from.

The DFT calculations are by far the most resource demanding step and we can decrease the computational load by using the same 3x3x5 atom-sized slab for multiple calculations of adsorption energies. In the present case each geometry optimized slab can be used for the calculation of adsorption energies of 9 different ontop sites and fcc hollow sites, respectively, saving almost half of the time-consuming geometry optimizations.

To make a regression model capable of predicting accurate adsorption energies in all parts of the composition space, it is natural to assume that the model must be trained on data sampled from different parts of the composition space. There are multiple ways to perform this sampling, both with and without bias. For this work we have chosen the elements based on prior chemical knowledge but settled on an unbiased sampling within that space: The composition of each slab is sampled from a Dirichlet distribution with  $\alpha = 1$  in order to sample points in the composition space with uniform probability. Consequently, a given slab might receive the composition  $Ag_{0.1}Ir_{0.0}Pd_{0.3}Pt_{0.2}Ru_{0.4}$  and each of the 45 atoms in the slab will be picked with the corresponding probability of each element. In figure 2, it is illustrated that a narrow sampling of equimolar composition will result in composition-wise very similar slabs. In contrast, the Dirichlet distribution can span the composition space in a uniform manner which will provide a much more diverse set of slabs. This could enhance the regression accuracy along edges and corners of the composition space, but one must also keep in mind that the equimolar slabs typically produce more complex binding sites that could be more difficult to model accurately. Hence, one could justify a weighted sampling scheme with a higher density towards the center of composition space corresponding to the increased diversity of the site motifs.



**Fig. 2** a) Illustration of a 3 dimensional simplex mapping the composition of 500 AgIrPdPt slabs of 45 atoms randomly drawn from an equimolar distribution. b) Similar illustration mapping the composition of 500 slabs of 45 atoms drawn from a Dirichlet distribution with  $\alpha$ =1. Points are coloured to represent ontop adsorption sites on different elements (ensembles) and some sample slabs are pictured.

## Adsorption energy distributions of the extended HEA surface

Having established an initial screening of adsorption energies, we are ready to set up a regression model to predict the adsorption energy of all possible site motifs of a Ag-Ir-Pd-Pt-Ru HEA. Considering the site geometry and element identities, the principal deciding factor for the adsorption energy is the identity of the atoms directly involved in the bond e.g. the adsorption energies of \*O bound to fcc hollow sites constituted of Ir<sub>2</sub>Pd will be fairly similar. These archetype motifs are known as ensembles [23,35] and can be viewed as discrete adsorption energies broadened to Gaussian-like distributions of adsorption energies by the electronic effect of the local atomic environment surrounding the binding site. This broadening is also referred to as the ligand effect. As seen in figure 3, these ensembles change shape and sometimes position when we adjust the alloy composition and this is a challenging factor for regression models.



**Fig. 3** a) Histogram showing the density of 1899 DFT adsorption energies of ontop \*OH on the fcc(111) facet of equimolar Ag-Ir-Pd-Pt-Ru relative to Pt(111). b) Histogram of 441 adsorption energies of equimolar IrPdPtRu. c) Histogram of 498 adsorption energies of equimolar IrPt. Dashed lines outline the shape of the quinary alloy distribution.

Earlier, we have successfully employed a multiple linear least squares fit for each unique ensemble to predict adsorption energies based on a zone-reduced features of the site motifs [22, 36]. However, this approach ignores possible position-related correlations in adsorption energy, and training data can become scarce with an increased number of dimensions due to piecewise modeling (see supporting information). Therefore, we have progressed to more

advanced machine learning algorithms, namely graph convolutional neural networks, which have recently gained positive attention within computational materials science due to the graph-type features being naturally suited to represent atomic scale systems [37-39].

When reducing the positional information of the DFT simulated slab, only connectivity information and element identity is included. Several other state-of-the-art models utilize bond lengths [40,41], however, these are not available when predicting the adsorption energy of non-relaxed adsorption sites, hence this information is excluded. We do, however, include which layer each atom inhabits and a feature indicating if next-nearest neighboring atoms have a direct vector through a neighboring atom to the ensemble atoms. This will allow distinction between two important atomic positions in the third layer [29] and was found to enhance regression accuracy.

The graph-type features consist of a list of atoms, up to the next-nearest neighboring atoms of the ensemble (figure S2) where the elemental-identity of each atom is one-hot encoded along with a layer number and the aforementioned feature. This totals to a 9-dimensional feature vector for each atom. In addition, a sparse adjacency matrix denotes the connectivity between atoms as defined by element-based cut-off radii.

Convolutional neural networks are customizable, diverse and in constant development, so optimization of the architecture can be a challenge in itself. Initial screening revealed gated graph convolutional networks, which is a subtype of recurrent networks utilizing gated recurrent unit (GRU) cells [42], to obtain good regression accuracy on our data. The suitability of this type of convolution could stem from comprehension of some sequential structure in the propagation of relevant electronic effects in the local atomic environment. Equivalently, not every atomic position is of equal importance to the adsorption energy and therefore a trainable global pooling scheme weighs graph output based on post-convolution atom features.



**Fig. 4** Overview of the adsorption energy regression procedure. **a)** Histogram of DFT calculated adsorption energies of ontop \*OH on the fcc(111) facet of equimolar Ag-Ir-Pd-Pt-Ru relative to Pt(111). **b)** Local atomic environment of the binding site represented by the 3x3x5 atom-sized slab with periodic lateral boundaries. The feature processing simplifies the atom positions and identities into a graph-type feature including up to the next nearest atomic neighbor of the ensemble atoms. **c)** Schematic drawing of the graph convolutional neural network architecture. **d)** Predicted adsorption energy distributions of 10<sup>6</sup> random ontop \*OH sites of equimolar Ag-Ir-Pd-Pt with a gradual change from Ag-rich to Ru-rich.

We trained the network on the dataset sampled uniformly in composition space, whilst validating and testing on two composite datasets with samples from several different alloy compositions to assure a good prediction accuracy across all possible binding site motifs. A grid search of convolution layer depth, width and hidden layers was performed as seen in table S1. It was observed that 3 convolution layers is enough to capture the information of the binding site, which is to be expected as 3 layers allow message passing between all atoms, except between the hydrogen of \*OH and the next-nearest neighbors which are four bonds apart. Subsequent investigation revealed that a higher number of feature dimensions is generally beneficial and, therefore, each atom feature vector was padded with additional zeros to allow higher-dimensional features to be expressed during convolution. Surprisingly, post-pooling hidden layers did not improve the model and a single multiple linear output layer proved sufficient. This resulted in a very lean and minimal network architecture with only 3062 adjustable weights and biases.

The optimized model achieved a validation mean absolute error (MAE) of 61 meV as seen in figure 5a and a combined test MAE of 62 meV as seen in figure 5c and 5d. This is a 25% decrease over our previous linear regression model as shown in table S2 and figure S3. To gain insight into the convolution process we can perform principal component analysis on the pooled graph feature vectors. Normally, clustering algorithms e.g. t-distributed stochastic neighbor embedding (t-SNE) is suited for such an analysis, but because our model does not include any non-linear structure, post-pooling it is innately trained to output linearly correlated features. This is evident from figure 5b, where the first and second principle components (PCs) show a distinct separation of ontop \*OH sites and fcc hollow \*O sites. We

observe the presence of strong binding elements in the ensemble by its position in the principle component space e.g. Ru containing fcc hollow ensembles are found at negative values of PC1 while  $Pd_3$  and  $Ag_3$ , of which there are few, are found at positive values of PC1.



**Fig. 5** a) Curve showing the decreasing MAE/L1Loss on the training and validation. The epoch with lowest validation error is circled. b) Principal component analysis of all training samples after applying convolutional and pooling layers of the trained graph convolutional neural network. Samples are plotted as dots in the space spanned by the first and second components with 49% and 14% explained variance ratio, respectively. Samples are coloured according to DFT calculated adsorption energy with ontop \*OH being blue/green and fcc hollow \*O sites being red/yellow. The composition of adsorption site ensembles generally transition from the strong to the weak binding elements along the arrow with element labels. **c-d)** Parity plots with predicted adsorption energy plotted against the target DFT calculated adsorption energy for the testset samples. Ontop \*OH sites are plotted in light blue and fcc hollow \*O are plotted in dark red. A histogram of the errors showing the centering of predictions is shown with solid and dashed lines indicating perfect agreement and +/- 0.1 eV error, respectively.

For future applications it is convenient to know the required amount of training data necessary to achieve good regression performance. Therefore, a learning curve was constructed by an 80/20 splitting of all available data into training and validation sets and subsequently training the neural network on subfractions of the training set. An MAE of 60 meV is almost already achieved at a training set size of 2500 adsorption energies as shown in figure S4 and converges at around 53 meV. Compared to other contemporary work, this is very accurate for such small training sets and lean network architecture [37,43], but we must

also keep in mind that this is only within five surface elements, two unique adsorbates and a single facet. From figure S5 it is also apparent that at a lower training set size (<5000 samples) the model is transferring learned trends between ontop \*OH and fcc \*O sites i.e. there is a benefit to training a combined model on both instead of training a separate model for each.

In the context of this work, the application of this regression model is prediction of adsorption energy distributions. Therefore, another useful comparison is how well the regression model recreates the distributions as it forgives the individual errors in favor of how well the shape and position of the distributions is predicted. To this end, we apply two-sample Kolmogorov-Smirnov (KS) tests to compare the DFT calculated adsorption energy distributions of ontop \*OH and fcc hollow \*O to the predicted distributions as seen in figure S6. This yields the probability of the distributions being drawn from the same underlying continuous distribution but as the KS test is quite sensitive to small deviations, we bootstrap the test across many simulated distributions and analyze the median p-value. As seen in table S3, the two-sample KS tests reveals that our previously used linear models actually does an admirable job in recreating the adsorption energy distributions of quinary and quaternary alloys making it a viable alternative to more complex models even though the neural network outperforms them on the binary alloys.

# Net adsorption

With a trained regression method it is now possible to predict the adsorption energy distribution of a hypothetical HEA surface given a set of molar fractions of constituent metals. Assuming that the randomly arranged surface atoms would be found with the same frequency as the alloy composition it would be a matter of weighing the possible adsorption site motif with the probability of such a site being found on the surface. However, the diversity of binding sites, spectator species and the competitive co-adsorption of reaction intermediates will perturb the expected adsorbate coverage of the HEA surface. To obtain the *net adsorption energy distribution*, these perturbing factors must be accounted for along with the mutual interaction of adsorbates. The net adsorption energy distribution represents the available sites, which is the part of the surface actually doing the catalysis, taking into account that all stronger binding sites are already occupied.

We found that an effective and intuitive solution was to simulate an *NxNx*3-sized HEA fcc(111) surface with atoms randomly picked, when given the desired molar ratios. With *N*=96 this gives  $\sim 10^5$  motifs of ontop sites and fcc hollow sites, respectively, which subsequently are marked with the expected adsorption energy by the regression algorithm. This constitutes the *gross adsorption energy distribution*.

We assume the free energy of adsorption to be function of potential written as  $\Delta G_{*_{OH}}(U) = \Delta G_{*_{OH}}(0) - eU$ , and for \*O as  $\Delta G_{*_{O}}(U) = \Delta G_{*_{O}}(0) - 2eU$ . Setting  $\Delta G(U) = 0$ , this means that adsorption will happen when  $\Delta G_{*_{OH}}(0) = \frac{1}{2}\Delta G_{*_{O}}(0) = eU$ . As we increase U in our potential sweep, we can then detect when either  $\Delta G_{*_{OH}}(0)$  or  $\frac{1}{2}\Delta G_{*_{O}}(0)$  become equal to eU, and when they do, an adsorption happens. In this fashion, each adsorption site is occupied from most to least stable during an electrochemical potential sweep after halving all fcc \*O adsorption energies.

Starting with the single strongest binding site, a corresponding adsorbate is added to the surface. To emulate the observed adsorbate coverages at the interface [44,45], we impose restrictions to the adsorption behavior of each adsorbate by ensuring that no surface atom is bonded to more than one adsorbate. This imposes a maximum coverage of 1/3 monolayer (ML) \*O [46-48]. Adsorption of \*OH next to an already adsorbed \*OH, will cause their shared neighboring ontop sites to be blocked as seen in figure 5d and figure S7. This promotes a hexagonal-like adsorption pattern of \*OH with a maximum coverage of 2/3 ML \*OH at ontop sites, mimicking the inter-adsorbate hydrogen bonding [49,50] (see supporting information).

This maximum coverage of \*OH is not equal to the previously reported 5/12 ML \*OH [44-45, 51], due to this coverage limit being specific for \*OH formation on Pt(111) surface. The HEA surface, however, is made up of multiple elements, creating continuity in stable surface states. The limits of 1/3 and 2/3 for \*O and \*OH, respectively, are not crucial for the activity calculation as sites with a weak adsorption only contribute very little to the activity. Thus, the results are not sensitive to this assumption. However, the limits ensure that the surfaces look realistic and as the complete \*OH coverage has the same charge as the complete \*O coverage, the relative stability of the two coverages will not change with potential.

As seen in figure 5a-f the process of adding adsorbates is repeated until no sites are available and the resulting population of occupied sites will constitute the net adsorption energy distribution. It is visibly different from the gross distribution as seen in figure 5g and 5h since the competitive co-adsorption of both species have lowered adsorbate coverage significantly.



**Fig. 6 a)** Illustration of a local atomic surface environment of the HEA fcc(111) surface. **b-e)** Colored overlay showing the predicted adsorption energy with strong to weak binding sites coloured from blue to red. As binding sites are occupied, adjoining sites are blocked, indicated by black crosses. When adsorption of two adjoining \*OH adsorbates occur, the shared neighboring sites are blocked to mimic a hexagonal adsorption pattern as described in the main text. **f)** Adsorbates have been added in prioritized order until no more sites are available on the surface **g-h)** Net distributions of adjusted adsorption energies of ontop \*OH and fcc hollow \*O sites on the 96x96x3 atom-sized surface of  $Ag_{0.1} | r_{0.2} P d_{0.1} P t_{0.25} R u_{0.35}$ . Gross and net adsorption energy distributions are plotted as gray outlines and color-filled bars, respectively. Adsorbate coverages are plotted in green with the dashed lines denoting coverage without blocking and solid lines showing coverage with blocking.

## Catalytic activity measure

Having predicted the net adsorption energy distributions of adsorbates on the surface we link those distributions to an expected catalytic activity, which is kinetically modeled assuming the associative oxygen reduction with the following steps and Gibbs' free reaction energies:

$\Delta G_1 = \Delta G_{*OOH} - 4.92 \text{ eV} + \text{eU}$	(1)
$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OOH} + eU$	(2)
$\Delta G_3 = \Delta G_{*OH} - \Delta G_{*O} + eU$	(3)
$\Delta G_4 = -\Delta G_{*OH} + eU$	(4)
	$\Delta G_{1} = \Delta G_{*OOH} - 4.92 \text{ eV} + \text{eU}$ $\Delta G_{2} = \Delta G_{*O} - \Delta G_{*OOH} + \text{eU}$ $\Delta G_{3} = \Delta G_{*OH} - \Delta G_{*O} + \text{eU}$ $\Delta G_{4} = -\Delta G_{*OH} + \text{eU}$

where  $\Delta G_{*ads}$  is the adsorption energy of the corresponding adsorbate, e is the elementary charge and U the applied potential vs. the reversible hydrogen electrode (RHE). Assuming that one of these steps will be rate limiting we have the following Arrhenius-like term:

$$r = k \cdot e^{\frac{-\Delta G_{RLS}^*}{k_B T}}$$
(5)

with k being an pre-exponential factor,  $\Delta G_{RIS}^{\dagger}$  the Gibbs free energy of the transition state of the rate limiting step,  $k_{R}$  the Boltzmann constant and T the temperature, which we set to 298.15 K. By the Brøndsted-Evans-Polanyi relation [16,17], the Gibbs free energy of the transition state is related to the reaction energy by  $\Delta G^{\dagger} = \Delta G_{i} + C$  with C being some constant, thus, enabling substitution of  $\Delta G_{RLS}^{\dagger}$  in the Arrhenius term with  $\Delta G_{RLS}^{\dagger}$ . Due to the same-site linear scaling between \*OOH and \*OH [18,21,52]  $\Delta G_{*_{OOH}}$  can be approximated as  $\Delta G_{*OOH} \approx \Delta G_{*OH} + 3.2 \, eV$  and can reaction step 1 be expressed as  $\Delta G_1 \approx \Delta G_{*OH} - 1.72 \, eV + eU$ . Deeming step 1 and 4 to be potential limiting [20,53,54], the limiting reaction energy would be:

$$\Delta G_{RLS} = max(\Delta G_{1}, \Delta G_{4}) = max(\Delta G_{*OOH} - 4.92 \, eV, -\Delta G_{*OH}) + eU (6)$$
  
= max(\Delta G\_{\*OH} - 1.72 \end{v}, -\Delta G\_{\*OH}) + eU (7)  
= |\Delta G\_{\*OH} - 0.86 \end{v}| - 0.86 \end{v} + eU (8)

As the 0.86 eV is a direct consequence of the scaling between the adsorption energies of \*OH and \*OOH, it is not likely to change due to different DFT functionals or inclusion of interactions with the environment. In this way, the cancellation of errors between \*OH and \*OOH calculations and between \*OH calculations on different surfaces are utilized. Additionally, it is assumed that the interaction with the electrochemical environment on all sites is identical to that of Pt(111).

To evaluate fcc hollow sites occupied by \*O we assume that the activity can be estimated by considering two simultaneous proton and electron transfers to form water (eq. 3 and 4). This is an upper bound to the activity of the oxygen sites where the lower bound would be assuming that oxygen is an inactive spectator.

The optimum catalytic activity at an adsorption energy of 0.86 eV has been observed to be 0.1 and 0.2 eV larger than \*OH and \*O on Pt(111), respectively [53,55]. Therefore, as all reaction energies are kept relative to a pure Pt(111) surface, we have  $|\Delta G_{*OH} - 0.86 eV| = |\Delta G_{*OH} - (\Delta G_{*OH}^{Pt(111)} + 0.1 eV)| = |\Delta G_{*OH} - \Delta G_{*OH}^{Pt(111)} - 0.1 eV|$  In

conclusion, we obtain the following expression for the kinetic limitation current for binding site *i*:

$$j_{k,i} = k \cdot e^{\frac{-|\Delta G_{v_{0H}}^{i} - \Delta G_{v_{0H}}^{P(111)} - 0.1eV| + 0.86 eV - eU}{k_{B}T}} (9)$$

$$j_{k,i} = k \cdot e^{\frac{-0.5 \cdot |(\Delta G_{v_{0}}^{i} - \Delta G_{v_{0}}^{P(111)}) - 0.2eV| + 0.86 eV - eU}{k_{B}T}} (10)$$

When inserted into the Koutecký-Levich equation, a measure of the per-site current,  $j_i$ ,

measured in arbitrary units is obtained. This current is subsequently averaged across all *N* sites yielding the mean current density of the surface which can subsequently be corrected for surface mass transport:

$$j = \frac{1}{N} \sum_{i}^{N} j_{i} = \frac{1}{N} \sum_{i}^{N} \frac{1}{\frac{1}{j_{d}} + \frac{1}{j_{ki}}}$$
(11)

The parameter  $j_d$  represent local mass transport limitation and is set to unity.

This completes the procedure of predicting the net adsorption energy distributions to then evaluate the expected change in current density at a given potential relative to a pure Pt(111) surface. Screening the catalytic activity of a single alloy composition in this way can now be done within a timeframe of seconds.

## Optimization and search in the composition space

Having established a procedure that can give an estimate of catalytic activity for a specific alloy composition, we now apply that capability to search the composition space for the alloy composition that maximizes catalytic activity.

When the space is relatively low-dimensional like the present example of 5 elements it is reasonable to do activity predictions of all points on a coarse grid with a resolution of 5% steps. As the activity across the hyperplane resembles a smooth function, such a grid search would likely identify the approximate global optimum and then subsequently be refined through experiments. However, in a higher-dimensional space a more efficient search strategy is needed and for this purpose we have chosen to employ a Bayesian optimization algorithm that drastically minimizes the amount of calls made to the activity prediction procedure.

As described in previous work [36], we employ Gaussian process regression as the surrogate function and expected improvement [56] for the acquisition function. From a small number of initial sampled compositions the surrogate function is fitted. It is then used to evaluate the acquisition function at a number of random compositions and subsequently find the global acquisition optimum at a resolution of 1%. This optimum composition is then sampled with activity prediction procedure and the surrogate function is refitted including the newly sampled point. As there can be a sizable error in individual adsorption energy predictions, we bound the search to a single element maximum content of 80 atomic percent

(at.%). This prevents the search from sampling close to the pure elements which could result in an erroneous activity estimate.

From this search, we very quickly obtain an optimum activity estimate at varying compositions of Ag-Pd as listed in table S4. As seen in figure 6a, this is natural since the ontop \*OH adsorption of the Pd ensemble is very close to the optimum adsorption energy. Hence, one could expect to see an increase in activity with increased Pd content, but \*O bound to fcc hollow Pd<sub>3</sub>-sites is slightly more stable than Pd bound \*OH. Therefore, increased Pd content also result in higher \*O coverage, which does not contribute as much to the catalytic activity. These two counteracting effects result in a rather unchanged activity estimate from ~40 at.% to ~80 at.% Pd where we estimate a roughly 7-fold increase in activity (measured as the current density at 0.820 V vs. RHE) compared to a pure Pt(111) surface. As we approach pure Pd, we would expect a rapid decline in activity when the adsorbate coverage almost exclusively consists of \*O. This highlights the role of Ag as inert adsorption sites that perturb the otherwise dominant adsorption pattern of \*O. Furthermore, this shows why the AgPd edge of the five dimensional composition space displays the highest predicted catalytic activity, as any other binary alloy in this space will have strongly adsorbing ensembles that will block most of the potential active sites. One such example is the Ir-Pt edge where Pt-bound \*OH will have a near-optimum adsorption energy due to favorable ligand effects but most of the surface will be occupied by \*OH bound to Ir-ensembles. We remark that both of these binary alloys have previously been identified to exhibit enhanced activity as catalysts for ORR [36,57,58].



**Fig. 7** Distributions of adjusted adsorption energies of ontop \*OH and fcc hollow \*O sites on a 96x96x3 atom-sized surface of **a**) Ag<sub>0.5</sub>Pd<sub>0.5</sub> and **c**) Ir<sub>0.5</sub>Pt<sub>0.5</sub>. Gross and net adsorption energy distributions are plotted as gray outlines and color-filled bars, respectively. Adsorbate coverages are plotted in green and the normalized  $j_{k,i}$ 

-term (eq. 10) as a function of adsorption energy is plotted in dashed black lines. Illustration of 12x12x3 atom-sized surfaces of **b**)  $Ag_{0.5}Pd_{0.5}$  and **d**)  $Ir_{0.5}Pt_{0.5}$ , showing example adsorption patterns of \*OH and \*O. Grey atoms represent Pd or Pt, blue atoms represent Ag or Ir, red atoms represent oxygen and white atoms represent hydrogen.

# Conclusion

With this work, we have shown our current *modus operandi* for obtaining estimates of catalytic activity for an HEA surface of any composition within a predefined composition space from first principle calculations. We have discussed some of the modeling choices taken along the way and successfully identified favorable binary alloys, which have previously been observed to have good catalyst performance.

We stress that this is a flexible framework where the choices can be altered to suit the reaction, surface or composition space of interest and that computational screening of HEA catalysts will be in constant development. We propose that the core differences between highly disordered HEA surfaces and ordered surfaces of pure metals and intermetallics, e.g. net adsorption energy distributions, must play a key role in assertion of catalytic properties. Therefore, understanding the shape and form of these distributions and how they couple with observed catalytic activity is paramount to HEA catalyst discovery as well as efficient modeling choices to achieve results within a reasonable timeframe.

# Computational information

### Density functional theory calculations

Density functional theory using the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional [59] as implemented in the GPAW code [60,61] was used to obtain \*OH and \*O adsorption energies on the fcc(111) surface with structures being set up and manipulated in the Atomic Simulation Environment (ASE) [62]. The quinary Ag-Ir-Pd-Pt-Ru alloy and the quaternary sub alloys were represented as 3x3x5 atom-sized surface slabs and a vacuum of 10.0 Å was added above and below the slab. The binary alloys were 3x4x5 atom-sized with a vacuum of 7.5 Å. Pt(111) references were made for both sizes. All slabs were constructed with an fcc lattice constant set to the weighted average of the calculated fcc lattice constants of the elements in the surface layer and simulated with periodic lateral boundaries. The atoms in the two bottom layers were held fixed and the structures were optimized until the maximum force on any atom was below at least 0.1 eV/Å. The wave functions were expanded in plane waves with an energy cutoff set to 400 eV, and the Brillouin zone was sampled with a Monkhorst-Pack grid [63] of 4x4x1 k-points. After geometry optimization the adsorption energies were calculated as:

$$\Delta E_{*ads}^{DFT} = \Delta E_{HEA+ads}^{DFT} - \Delta E_{HEA}^{DFT} - \Delta E_{Pt(111)+ads}^{DFT} + \Delta E_{Pt(111)}^{DFT}$$

with  $\Delta E_{HEA+ads}^{DFT}$  and  $\Delta E_{HEA}^{DFT}$  being the calculated total energy of the HEA slab with and without adsorbate, respectively.  $\Delta E_{Pt(111)+ads}^{DFT}$  and  $\Delta E_{Pt(111)}^{DFT}$  is the calculated total energy of the Pt(111) reference slab, also with and without adsorbate.

To generate the DFT data sets the atoms constituting the slab were drawn from a uniform distribution with equal probabilities of the included elements, either Ag-Ir-Pd-Pt-Ru or the quaternary sub alloys. Exceptions to this are the Dirichlet sampled dataset where each slab had its own set of probabilities drawn from a Dirichlet distribution with uniform density in the 5-dimension simplex space ( $\alpha$ =1) and the atom identities were subsequently picked from that set of probabilities. The binary alloys were sampled by randomly picking from all possible layouts of ensemble and nearest neighbors and randomly sampling remaining atoms with equal probability between the two elements. For the Dirichlet sampled dataset each unique slab was used for 9 adsorbate calculations of ontop \*OH and fcc hollow \*O, respectively.

## Data and feature processing

The optimized geometries were converted to graph-type features by the use of ASE's geometry tools to map out the adjacency of atoms. Cut-off radii were determined as the covalent radii of each element [64]. To exclude slabs that converged in a rearranged state or where the adsorbate jumped to a different site e.g. bridge or hcp hollow, graphs were excluded if they did not match the expected number of surface atoms in the ensemble and nearest neighbors combined. After preprocessing, the distribution of samples were as follows (number of ontop \*OH  $\Delta E_{DFT}$  / fcc hollow \*O  $\Delta E_{DFT}$ ): Dirichlet-sampled Ag-Ir-Pd-Pt-Ru (2519/2520), Ag-Ir-Pd-Pt-Ru (1899/1809), Ir-Pd-Pt-Ru(441/482), Ag-Pd-Pt-Ru(466/447), Ag-Ir-Pt-Ru(455/464), Ag-Ir-Pd-Ru(444/426), Ag-Ir-Pd-Pt(470/475), Ag-Pd(468/497), Ir-Pd(449/480), Ir-Pt(498/500), Pd-Ru(493/481) and Pt-Ru(349/489).

#### Training and validation of regression model

The graph convolutional neural network was set up within the pyTorch [65] framework. Each training procedure utilized the AdamW optimizer [66] (betas=(0.9, 0.999),eps=10<sup>-8</sup>,weight\_decay=0.01) with mean squared error (MSE) as loss function. The gridsearch of network architecture had a learning rate of  $2 \cdot 10^{-3}$  and batch size 128. Subsequently, learning rate was dropped to  $1 \cdot 10^{-3}$  and batch size to 64 for training the final models. After each epoch, the rolling mean ( $\pm 10$  epochs) of the validation error was compared to all prior epochs excluding the newest 100 (patience of 100 epochs). If the rolling mean validation error had not decreased by at least 1% compared to the previous lowest error early stopping was evoked and the model weights with the lowest validation error were chosen for the trained model.

### Net adsorption simulation

To simulate the extended HEA surface each surface atom was emulated by the element label in an array location. Thus, a 3-dimensional array of size NxNx3 simulates the corresponding NxNx3 surface. By allocating the predicted surface atoms adsorption energy to their corresponding array indices, we obtained a gross adsorption grid. The net adsorption was then obtained by iterating through the gross adsorption energy grid and masking select indices. In addition, a corresponding NxN boolean adsorption grid was constructed to keep track of which masked elements were masked due to an adsorption and which elements were masked due to blocking. The net adsorption energies are easily extracted by returning the gross adsorption energy grid values masked by the adsorption grid.

#### Bayesian optimization procedure

The Bayesian optimization of HEA composition is described in earlier work [36] but briefly described a Gaussian process (GP) regressor with a weighted radial basis function kernel is fitted to 5 randomly picked compositions and their predicted catalytic activity. The GP regressor is then used to evaluate the expected improvement acquisition value [56] for 10<sup>3</sup> random compositions from which the highest valued composition is found by local optimization in step sizes of 1%. The catalytic activity prediction for the acquisition optimum composition is subsequently added to the sampled points and the GP regressor is refitted. This procedure was repeated 45 times in this work.

#### References

[1] Xie, P., Yao, Y., Huang, Z., Liu, Z., Zhang, J., Li, T., Wang, G., Shahbazian-Yassar, R., Hu, L., Wang, C.: Highly efficient decomposition of ammonia using high-entropy alloy catalysts. Nat. Comm. 10(1), 1-12 (2019)

[2] Zhan, C., Xu, Y., Bu, L., Zhu, H., Feng, Y., Yang, T., Zhang, Y., Yang, Z., Huang, B., Shao, Q., Huang, X.: Subnanometer high-entropy alloy nanowires enable remarkable hydrogen oxidation catalysis. Nat. Comm. 12(1), 1-8 (2021)

[3] Zhang, G., Ming, K., Kang, J., Huang, Q., Zhang, Z., Zheng, X., Bi, X.: High entropy alloy as a highly active and stable electrocatalyst for hydrogen evolution reaction. Electrochim. Acta 279, 19-23 (2018)

[4] Nellaiappan, S., Katiyar, N.K., Kumar, R., Parui, A., Malviya, K.D., Pradeep, K.G., Singh, A.K., Sharma, S., Tiwary, C.S., Biswas, K.: High-entropy alloys as catalysts for the CO2 and CO reduction reactions: Experimental realization. ACS Catal. 10(6), 3658-3663 (2020)

[5] Li, S., Tang, X., Jia, H., Li, H., Xie, G., Liu, X., Lin, X., Qiu, H.J.: Nanoporous high-entropy alloys with low Pt loadings for high-performance electrochemical oxygen reduction. J. Catal. 383, 164-171 (2020)

[6] Wu, D., Kusada, K.,Yamamoto, T., Toriyama, T., Matsumura, S., Kawaguchi, S., Kubota, Y., Kitagawa, H.: Platinum-Group-Metal High-Entropy-Alloy Nanoparticles. J. Am. Chem. Soc., 142, 32, 13833–13838 (2020)

[7] Wu, D., Kusada, K., Nanba, Y., Koyama, M., Yamamoto, T., Toriyama, T., Matsumura, S., Seo, O., Gueye, I., Kim, J., Kumara, L., Sakata, O., Kawaguchi, S., Kubota, Y., Kitagawa, H.: Noble-Metal High-Entropy-Alloy Nanoparticles: Atomic-Level Insight into the Electronic Structure. J. Am. Chem. Soc., 144, 8, 3365–3369 (2022) [8] Sabatier, P.: La Catalyze En Chimie Organique, Encyclopédie de Chimique Appliquée (1913)

[9] Kluender, E. J., Hedrick, J. L., Brown, K. A., Rao, R., Meckes, B., Du, J. S., Moreau, L. M., Mirkin, C. A.: Catalyst discovery through megalibraries of nanomaterials. PNAS 116(1), 40-45 (2019)

[10] Yao, Y., Huang, Z., Li, T., Wang, H., Liu, Y., Stein, H. S., Mao, Y., Gao, J., Jiao, M., Dong, Q., Dai, J., Xie, P., Xie, H., Lacey, S. D., Takeuchi, I., Gregoire, J. M., Jiang, R., Wang, C., Taylor, A. D., Shahbazian-Yassar, R., Hu, L.: High-throughput, combinatorial synthesis of multimetallic nanoclusters. PNAS 117(12), 6316-6322 (2020)

[11] Banko, L., Krysiak, O.A., Pedersen, J.K., Xiao, B., Savan, A., Löffler, T., Baha, S., Rossmeisl, J., Schuhmann, W., Ludwig, A.: Unravelling Composition–Activity–Stability Trends in High Entropy Alloy Electrocatalysts by Using a Data-Guided Combinatorial Synthesis Strategy and Computational Modeling. Adv. Energy Mater., 2103312 (2022)

[12] Pedersen, J.K., Batchelor, T.A.A., Bagger, A., Rossmeisl, J.: High-Entropy Alloys as Catalysts for the CO<sub>2</sub> and CO Reduction Reactions. ACS Catal., 10(3), 2169-2176 (2020)

[13] Bagger, A., Ju, W., Varela, A.S., Strasser, P., Rossmeisl, J.: Electrochemical CO<sub>2</sub> Reduction: A Classification Problem. Chem. Phys. Chem., 18(22), 3266-3273 (2017)

[14] Peterson, A.A., Nørskov, J.K.: Activity Descriptors for CO2 Electroreduction to Methane on Transition-Metal Catalysts. J. Phys. Chem. Lett., 3(2), 251-258 (2012)

[15] Hori, Y., Wakebe, H., Tsukamoto, T., Koga, O.: Electrocatalytic Process of CO Selectivity in Electrochemical Reduction of CO2 at Metal Electrodes in Aqueous Media. Electrochimica Acta., 39(11-12), 1833-1839 (1994)

[16] Brønsted, N.: Acid and Basic Catalysis. Chem. Rev. 5, 231 (1928)

[17] Evans, M.G., Polanyi, N.P.: Inertia and driving force of chemical reactions. Trans. Faraday Soc. 34, 11-24 (1938)

[18] Nørskov, J.K., Bligaard, T., Logadottir, A., Bahn, S., Hansen, L.B., Bollinger, M., Bengaard, H., Hammer, B., Sljivancanin, Z., Mavrikakis, M., Xu, Y., Dahl, S., Jacobsen, C.J.H.: Universality in heterogeneous catalysis. J. Catal. *209*(2), 275-278 (2002)

[19] Abild-Pedersen, F., Greeley, J., Studt, F., Rossmeisl, J., Munter, T.R., Moses, P.G., Skulason, E., Bligaard, T., Nørskov, J.K.: Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces. Phys. Rev. Lett. 99(1), 016105 (2007)

[20] Rossmeisl, J., Logadottir, A., Nørskov, J.K.: Electrolysis of water on (oxidized) metal surfaces. Chem. Phys., 319(1-3), 178-184 (2005)

[21] Pedersen, J.K., Batchelor, T.A.A, Yan, D., Skjegstad, L.E.J., Rossmeisl, J.: Surface electrocatalysis on high-entropy alloys. Curr Opin Electrochem 26, 100651 (2021)

[22] Batchelor, T.A.A., Pedersen, J.K., Winther, S.H., Castelli, I.E., Jacobsen, K.W., Rossmeisl, J.: High-entropy alloys as a discovery platform for electrocatalysis. Joule 3(3), 834-845 (2019)

[23] Löffler, T., Ludwig, A., Rossmeisl, J., Schuhmann, W.: What Makes High-Entropy Alloys Exceptional Electrocatalysis. Angew. Chem. Int. Ed., 60(52), 26894–26903 (2021)

[24] Rossmeisl, J., Karlberg, G.S, Jaramillo, T., Nørskov, J.K.: Steady state oxygen reduction and cyclic voltammetry. Faraday Discuss., 140, 337-346 (2008)

[25] Batchelor, T.A.A., Löffler, T., Xiao, B., Krysiak, O.A., Strotkötter, V., Pedersen, J.K., Clausen, C.M., Savan, A., Li, Y., Schuhmann, W., Rossmeisl, J., Ludwig, A.: Complex-Solid-Solutions Electrocatalyst Discovery by

Computational Prediction and High-Throughput Experimentation. Angew. Chem. Int. Ed., 60(13), 6932-6937 (2020)

[26] Wu, D., Kusada, K., Yamamoto, T., Toriyama, T., Mutsumara, S., Gueye, I., Seo, O., Kim, J., Hiroi, S., Sakata, O., Kawaguchi, S., Kuboto, Y., Kitagawa, H.: On the electronic structure and hydrogen evolution reaction activity of platinum group metal-based high-entropy-alloy nanoparticles. Chem. Sci., 11(47), 12731-12736 (2020) [27] Nørskov, J.K., Rossmeisl, J., Logadottir, A., Lindqvist, L., Kitchin, J.R., Bligaard, T., Jónsson.: Origin of the

Overpotential at a Fuel-Cell Cathode. J. Phys. Chem. B, 108(46), 17886–17892 (2004) [28] Divanis, S., Kutlusoy, T., Boye, I.M.I., Man, I.C., Rossmeisl, J.: Oxygen evolution reaction: a perspective on a

decade of atomic scale simulations. Chem. Sci., 11(11), 2943-2950 (2020)

[29] Clausen, C.M., Batchelor, T.A., Pedersen, J.K., Rossmeisl, J.: What Atomic Positions Determines Reactivity of a Surface? Long-Range, Directional Ligand Effects in Metallic Alloys. Adv. Sci. 8(9), 2003357 (2021)

[30] Clausen, C.M., Pedersen, J.K., Batchelor, T.A., Rossmeisl, J.: Lattice distortion releasing local surface strain on high-entropy alloys. Nano Res. 1-5 (2021)

[31] Wang, L., Zeng, Z., Gao, W., Maxson, T., Raciti, D., Giroux, M., Pan, X., Wang, C., Greeley, J.: Tunable intrinsic strain in two-dimensional transition metal electrocatalysts. Science, 363(6429), 870-874 (2019)

[32] Escudero-Escribano, M., Malacrida, P., Hansen, M.H., Vej-Hansen, U.G., Velázquez-Palenzuela, A., Tripkovich, V., Schiøtz, J., Rossmeisl, J., Stephens, I.E.L., Chorkendorff, I.: Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction. Science, 352(6281), 73-76 (2016)

[33] Mavrikakis, M., Hammer, B., Nørskov, J.K.: Effect of Strain on the Reactivity of Metal Surfaces. Phys. Rev. Lett., 81(13), 2819 (1998)

[34] Vegard, L.: Die konstitution der mischkristalle und die raumfüllung der atome. Z. Phys. 5, 17. (1921)

[35] Li, H., Shin, K., Henkelman, G.: Effects of ensembles, ligand, and strain on adsorbate binding to alloy surfaces. J. Chem. Phys., 149(17), 174705 (2018)

[36] Pedersen, J.K., Clausen, C.M., Krysiak, O.A., Xiao, B., Batchelor, T.A., Löffler, T., Mints, V.A., Banko, L., Arenz, M., Savan, A., Schuhmann, W., Ludwig, A., Rossmeisl, J.: Bayesian Optimization of High-Entropy Alloy Compositions for Electrocatalytic Oxygen Reduction. *Angew. Chem.* 133(45), 24346-24354 (2021)

[37] Fung, V., Zhang, J., Juarez, E., Sumpter, B.G.: Benchmarking graph neural networks for materials chemistry. Npj Comput. Mater. 7(1), 1-8 (2021)

[38] Gilmer, J., Schoenholz, S.S., Riley, P.F., Vinyals, O., Dahl, G.E.: Neural Message Passing for Quantum Chemistry. arxiv (2017). https://arxiv.org/abs/1704.01212v2

[39] Chen, C., Ye, W., Zuo, Y., Zheng, C., Ong, S.P.: Graph Networks as a Universal Machine Learning Framework for Molecules and Crystals. Chem. Mater., 31(9), 3564–3572 (2019)

[40] Xie, T., Grossman, J.C.: Crystal Graph Convolutional Neural Networks for an Accurate and Interpretable Prediction of Materials Chemistry. Phys. Rev. Lett., 120(14), 145301 (2018)

[41] Fung, V., Zhang, J., Juarez, E., Sumpter, B.G.: Benchmarking graph neural networks for materials chemistry. npj Comp. Mater. 7(1), 1-8 (2021)

[42] Li, Y., Tarlow, D., Brockschmidt, M., Zemel, R.: Gated graph sequence neural networks. arXiv (2015). https://doi.org/10.48550/arXiv.1511.05493

[43] Chanussot, L., Das, A., Goyal, S., Lavril, T., Shuaibi, M., Riviere, M., Tran, K., Heras-Domingo, J., Ho, C., Hu, W., Palizhati, A. Sriram, A., Wood, B., Yoon, J., Parihk, D., Zitnick, C.L., Ulissi, Z.: Open catalyst 2020 (OC20) dataset and community challenges. ACS Catal. 11(10), 6059-6072. (2021)

[44] Kristoffersen, H. H., Vegge, T., Hansen, H. A.: OH formation and H 2 adsorption at the liquid water–Pt (111) interface. Chemical science, 9(34), 6912-6921 (2018)

[45] Hansen, M.H., Nilsson, A., Rossmeisl, J.: Modelling pH and potential in dynamic structures of the water/Pt(111) interface on the atomic scale. Phys. Chem. Chem. Phys., 19(34), 23505-23514 (2017)

[46] Brown, W.A., Kose, R., King, D.A.: Femtomole Adsorption Calorimetry on Single-Crystal Surfaces. Chem. Rev., 98(2), 797-831 (1998)

[47] Miller, D.J., Öberg, H., Näslund, L.-Å., Anniyev, T., Ogasawara, H., Petterson, L.G.M., Nilsson, A.: Low O2 dissociation barrier on Pt(111) due to adsorbate–adsorbate interactions. J. Chem. Phys., 133(22), 224701 (2010)
[48] Miller, S.D., Kitchin, J.R.: Relating the coverage dependence of oxygen adsorption on Au and Pt fcc(1 1 1)

surfaces through adsorbate-induced surface electronic structure effects. Surf. Sci., 603(5), 794-801 (2009)

[49] Schiros, T., Näslund, L.-Å., Andersson, K., Gyllenpalm, J., Karlberg, G.S., Odelius, M., Ogasawara, H., Pettersson, L.G.M., Nilsson, A.: Structure and Bonding of the Water-Hydroxyl Mixed Phase on Pt(111). J. Phys. Chem. C, 111(41), 15003-15012 (2007)

[50] Schnur, S., Groß, A.: Properties of metal–water interfaces studied from first principles. New J. Phys., 11(12), 125003 (2009)

[51] Tripkovic, V., Vegge, T.: Potential- and Rate-Determining Step for Oxygen Reduction on Pt(111). J. Phys. Chem. C, 121(48), 26785–26793 (2017)

[52] Bligaard, T., Nørskov, J. K., Dahl, S., Matthiesen, J., Christensen, C. H., Sehested, J.: The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis. Journal of catalysis, 224(1), 206-217 (2004)

[53] Stephens, I. E., Bondarenko, A. S., Grønbjerg, U., Rossmeisl, J., Chorkendorff, I.: Understanding the electrocatalysis of oxygen reduction on platinum and its alloys. Energy Environ.Sci., 5(5), 6744-6762. (2012)

[54] Koper, M.T.M.: Thermodynamic theory of multi-electron transfer reactions: Implications for electrocatalysis. J. Electroanal. Chem., 660(2), 254-260 (2011)

[55] Greeley, J., Stephens, I. E. L., Bondarenko, A. S., Johansson, T. P., Hansen, H. A., Jaramillo, T. F., Rossmeisl, J., Chorkendorff, I, Nørskov, J. K.: Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. Nat. Chem., 1(7), 552-556 (2009)

[56] Jones, D.R., Schonlau, M., Welch, W.J.: Efficient Global Optimization of Expensive Black-Box Functions. J. Glob. Optim., 13(4), 455-492 (1998)

[57] Zeledón, J.A.Z., Stevens, M.B., Gunasooriya, G.T.K.K., Gallo, A., Landers, A.T., Kreider, M.E., Hahn, C., Nørskov, J.K., Jaramillo, T.F.: Tuning the electronic structure of Ag-Pd alloys to enhance performance for alkaline oxygen reduction. Nat. Comm., 12(1), 1-9 (2021)

[58] Ioroi, T., Yasuda, K.: Platinum-iridium as oxygen reduction electrocatalysts for polymer electrolyte fuel cells. J. Electrochem. Soc., 152(10), A1917 (2005)

[59] Hammer, B.H.L.B., Hansen, L.B., Nørskov, J.K.: Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. Phys. Rev. B 59(11), 7413 (1999)

[60] Mortensen, J.J., Hansen, L.B., Jacobsen, K.W.: Real-space grid implementation of the projector augmented wave method. Phys. Rev. B, 71(3), 035109 (2005)

[61] Enkovaara, J., Rostgaard, C., Mortensen, J.J., Chen, J., Dulak, M, Ferrighi, L., Gavnholt, J., Glinsvad, C., Haikola, V., Hansen, H.A., Kristoffersen, H.H., Kuisma, M., Larsen, A.H., Lehtovaara, L., Ljungberg, M., Lopez-Acevedo, O., Moses, P.G., Ojanen, J., Olsen, T., Petzold, V., Romero, N.A., Stausholm-Møller, J., Strange, M., Tritsaris, G.A., Vanin, M., Walter, M., Hammer, B., Häkkinen, H., Madsen, G.K.H., Nieminen, R.M., Nørskov, J.K. Puska, M., Rantala, T.T., Schiøtz, J., Thygesen, K.S., Jacobsen, K.W.: Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method. J. Phys.: Condens. Matter, 22(25), 253202 (2010)

[62] Larsen, A.H., Mortensen, J.J., Blomqvist, J., Castelli, I.E., Christensen, R., Dulak, M., Friis, M.G., Hammer, B:, Hargus, C., Hermes, E., Jennings, P.C., Jensen, P.B., Kermode, J., Kitchin, J., Kolsbjerg, E., Kubal, J., Kaasbjerg, K., Lysgaard, S., Maronsson, J.B., Maxson, T., Olsen, T., Pastewka, L., Peterson, A., Rostgaard, C., Schiøtz, J., Schütt, O., Strange, M., Thygesen, K.S., Vegge, T., Vilhelmsen, L., Walter, M., Zeng, Z., Jacobsen, K.W.: The Atomic Simulation Environment - A Python library for working with atoms. J. Phys.: Condens. Matter 29(27), 273002 (2017)

[63] Monkhorst, H.J., Pack, J.D., 1976. Special points for Brillouin-zone integrations. Phys. Rev. B 13(12), 5188 (1976)

[64] Cordero, B., Gómez, V., Platero-Prats, A. E., Revés, M., Echeverría, J., Cremades, E., Barragán, F., Alvarez, S.: Covalent radii revisited. Dalton Trans, (21), 2832-2838 (2008)

[65] Paszke, A., Gross, S., Massa, F., Lerer, A., Bradbury, J., Chanan, G., Killeen, T., Lin, Z., Gimelshein, N., Antiga, L., Desmaison, A., Kopf, A., Yang, E., DeVito, Z., Raison, M., Tejani, A., Chilamkurthy, S., Steiner, B., Fang, L., Bai, J., Chintala, S.: Pytorch: An imperative style, high-performance deep learning library. Adv. Neural Inf. Process. Syst. *32*. (2019)

[66] Loshchilov, I. and Hutter, F.: Decoupled weight decay regularization. arXiv (2017) https://doi.org/10.48550/arXiv.1711.05101